

THE MAXIMAL EXCESS CHARGE IN MÜLLER DENSITY-MATRIX-FUNCTIONAL THEORY

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ABSTRACT. We consider an atom described by Müller theory, which is similar to Hartree–Fock theory, but with a modified exchange term. We prove that a nucleus of charge Z can bind at most $Z + C$ electrons, where C is a universal constant. Our proof proceeds by comparison with Thomas–Fermi theory and a key ingredient is a novel bound on the number of electrons far from the nucleus.

1. INTRODUCTION

One of the central questions in mathematical atomic physics is how many electrons a nucleus can bind. Despite convincing experimental evidence that there can be only one or two excess electrons, even a uniform bound on the excess charge still eludes a rigorous mathematical proof. So far, this so-called ionization conjecture has only been proved in simplified models of an atom, namely the Thomas–Fermi model [7], the Thomas–Fermi–von-Weizsäcker model [13], the reduced Hartree–Fock model [14] and the (full) Hartree–Fock model [15]. In the latter two models the conjecture is settled in the weak form that there is a universal constant C such that the number of electrons bound by a nucleus of charge Z is at most $Z + C$. Recently, we were able to prove this also in the Thomas–Fermi–Dirac–von Weizsäcker model [4] and in this paper we will extend and generalize our method to treat the Müller model of an atom.

The Müller energy functional was introduced in [9] (see also [1]) and has received increasing interest in theoretical and computational quantum chemistry. For references and a systematic mathematical investigation we refer to [2]. Like Hartree–Fock and unlike Thomas–Fermi theory (and its relatives), Müller theory is a *density matrix* and not a density functional theory. This means that N -electron configurations are described by self-adjoint operators γ (*one-body density matrices*) on $L^2(\mathbb{R}^3)$ satisfying $0 \leq \gamma \leq 1$ and $\text{Tr } \gamma = N$. (For the sake of simplicity we ignore here the electron spin. Its inclusion would not change our results and methods qualitatively.) To each one-body density matrix γ , we can associate a density ρ_γ formally by $\rho_\gamma(x) = \gamma(x, x)$. (This definition can be made proper, for instance, using the spectral decomposition of the operator γ .) The energy in Müller theory is given by the functional

$$\mathcal{E}_Z^M(\gamma) = \text{Tr}(-\Delta\gamma) - \int_{\mathbb{R}^3} \frac{Z\rho_\gamma(x)}{|x|} dx + D(\rho_\gamma) - X(\gamma^{1/2}).$$

Here

$$D(\rho_\gamma) = \frac{1}{2} \iint_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\rho_\gamma(x) \rho_\gamma(y)}{|x - y|} dx dy$$

models the Coulomb repulsion between the electrons and

$$X(\gamma^{1/2}) = \frac{1}{2} \iint_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{|\gamma^{1/2}(x, y)|^2}{|x - y|} dx dy$$

models the exchange energy. The latter term, which involves the operator square root $\gamma^{1/2}$ of the operator γ , is the only, but important, difference to Hartree–Fock theory, where the exchange energy is modelled by $X(\gamma)$. We will review the heuristic reason for this choice at the end of the introduction. The ground state energy in Müller theory is given by

$$E_Z^M(N) = \inf \{ \mathcal{E}_Z^M(\gamma) \mid 0 \leq \gamma \leq 1 \text{ on } L^2(\mathbb{R}^3), \text{Tr } \gamma = N \}. \quad (1)$$

Here and in the following we do not need to assume that the parameters $Z > 0$ (the nuclear charge) and $N > 0$ (the number of electrons) are integers.

In [2], it was shown that the minimization problem $E_Z^M(N)$ has a minimizer if $N \leq Z$. It was also conjectured that for any $Z > 0$ there is a critical electron number $N_c(Z) < \infty$ such that $E_Z^M(N)$ has no minimizer if $N > N_c(Z)$. A simple by-product of our main result is a proof of this conjecture.

We shall prove

Theorem 1 (Ionization bound). *There is a constant $C > 0$ such that for all $Z > 0$, if the minimization problem $E_Z^M(N)$ in (1) has a minimizer, then $N \leq Z + C$.*

The basic strategy is to compare with Thomas–Fermi theory as in Solovej’s fundamental works [14] and [15]. Recall that in Thomas–Fermi theory, the ground state energy is obtained by minimizing the density functional

$$\mathcal{E}_Z^{\text{TF}}(\rho) = c^{\text{TF}} \int_{\mathbb{R}^3} \rho^{5/3}(x) dx - \int_{\mathbb{R}^3} \frac{Z\rho(x)}{|x|} dx + D(\rho)$$

with

$$c^{\text{TF}} = \frac{3}{5} (6\pi^2)^{2/3} \quad (2)$$

under the constraints

$$0 \leq \rho \in L^1(\mathbb{R}^3) \cap L^{5/3}(\mathbb{R}^3), \quad \int \rho = N.$$

(For comparison of our c^{TF} with the corresponding constant in [15] we note that in our definition of the Müller energy functional the kinetic energy is involves $-\Delta$, not $-(1/2)\Delta$, and that we ignore the electron spin.)

As in reduced and full Hartree–Fock theory we establish that certain quantities can be approximated by the corresponding quantities in Thomas–Fermi theory up to distances of order $o(1)$ away from the nucleus. This is remarkably far from the nucleus, since a priori, the standard Thomas–Fermi approximation is valid on distances of order $O(Z^{-1/3})$. In a certain sense our result shows that Müller theory belongs, like Thomas–Fermi–von Weizsäcker, Thomas–Fermi–Dirac–von Weizsäcker and reduced and full

Hartree–Fock theory, to a Thomas–Fermi universality class. A quantitative version of this universality property is the following basic comparison theorem between Müller and Thomas–Fermi theory.

Theorem 2 (Screened potential estimate). *Let γ_0 be a Müller minimizer for some $N \geq Z \geq 1$ and let $\rho_0 = \rho_{\gamma_0}$. Let ρ^{TF} be the Thomas–Fermi minimizer with $N = Z$. For every $r > 0$, define the screened nuclear potentials*

$$\Phi_r(x) = \frac{Z}{|x|} - \int_{|y| \leq r} \frac{\rho_0(y)}{|x-y|} dy, \quad \Phi_r^{\text{TF}}(x) = \frac{Z}{|x|} - \int_{|y| \leq r} \frac{\rho^{\text{TF}}(y)}{|x-y|} dy.$$

Then there are universal constants $C > 0$, $\varepsilon > 0$ such that

$$\left| \Phi_{|x|}(x) - \Phi_{|x|}^{\text{TF}}(x) \right| \leq C(|x|^{-4+\varepsilon} + 1)$$

for all $N \geq Z \geq 1$ and $|x| > 0$.

The significance of the power $|x|^{-4+\varepsilon}$ is that $\Phi_{|x|}^{\text{TF}}(x) \sim |x|^{-4}$ for $|x|$ small (see, e.g., [15]). Another consequence of this comparison is that the atomic radius of “infinite atoms” in Müller theory is very close to that in Thomas–Fermi theory. Similarly as in [15, Theorem 1.5], we have the following asymptotic estimate for the radii of “infinite atoms”.

Theorem 3 (Radius estimate). *Let γ_0 be a Müller minimizer for some $N \geq Z \geq 1$ and let $\rho_0 = \rho_{\gamma_0}$. For $\kappa > 0$, we define the radius $R(N, Z, \kappa)$ as the largest number such that*

$$\int_{|x| \geq R(N, Z, \kappa)} \rho_0(x) dx = \kappa.$$

Then there are universal constants $C > 0$, $\varepsilon > 0$ such that

$$\limsup_{N \geq Z \rightarrow \infty} \left| R(N, Z, \kappa) - B^{\text{TF}} \kappa^{-1/3} \right| \leq C \kappa^{-1/3-\varepsilon}$$

for all $\kappa \geq C$, where $B^{\text{TF}} = 5c^{\text{TF}}(4/(3\pi^2))^{1/3}$.

As we have already mentioned, Theorems 1 and 3 are straightforward consequences of Theorem 2. We establish the latter by Solovej’s ingenious bootstrap argument [14, 15], which he used to prove the ionization conjecture in reduced and full Hartree–Fock theory. The iterative step of this inductive proof relies on a bound on the number of electrons far away from the nucleus. Both in [14] and [15] this bound is derived by ‘multiplying the equation by $|x|$ ’, a fundamental strategy that goes back to Benguria and Lieb [5, Theorem 7.23], [6] (see also [10] for a modification of this strategy). Due to the presence of the exchange term, this strategy seems to fail both in Thomas–Fermi–Dirac–von Weizsäcker theory and in Müller theory (although it does work in Hartree–Fock theory), and this is probably the reason why even the problem of bounding the number of electrons has remained unsolved for so long in these models.

In [4], inspired by [11] and [3], we have developed a new strategy to obtain a bound on the number of electrons far away from the nucleus, which replaces the ‘multiplication by $|x|$ ’ strategy. While this new strategy was used in [11, 3, 4] only in the context of density functional theory, we demonstrate here that it can also be applied in density matrix theory. This argument

gives the a-priori bound $N \leq 2Z(1 + o(1))$ (see Lemma 8). Fortunately, just like the ‘multiplication by $|x|$ ’ strategy, it can also be applied to bound the number of electrons far away from the nucleus, which is the content of Lemma 7.

We end this introduction by listing some of the similarities and differences between Müller and Hartree–Fock theory; for proofs we refer to [2].

- (1) The Müller energy functional is convex in γ and strictly convex in ρ_γ , which shows, in particular, that the density of a minimizer is spherical symmetric. This property is shared by reduced Hartree–Fock theory, but not by full Hartree–Fock theory. Spherical symmetry leads to some minor simplifications in our argument, but we deliberately do not take advantage of these in order to emphasize the generality of our approach. We do, however, point out the places in the proofs where one could use spherical symmetry.
- (2) Electrons in Müller theory have a strictly negative self-energy. This phenomenon does not appear in (reduced or full) Hartree–Fock theory, but it does appear in Thomas–Fermi–Dirac–von Weizsäcker theory. While it has no direct consequences for us, it shows the delicate nature of the exchange term.
- (3) Since, for integer N , the Hartree–Fock minimizer is a projection (which is equal to its square root), the Müller ground state energy does not exceed the Hartree–Fock ground state energy.
- (4) The reason why $\gamma^{1/2}$ appears naturally in the exchange term can be seen from the following integral condition. While in Schrödinger theory the total Coulomb repulsion energy is modeled by the integral of $|x - y|^{-1}$ against the two-particle density, in Müller theory it is modeled by the integral against $(1/2)(\rho_\gamma(x)\rho_\gamma(y) - |\gamma^{1/2}(x, y)|^2)$. The latter expression, when integrated with respect to y , yields $((N - 1)/2)\rho_\gamma(x)$, which coincides with the value that the two-particle density of any state would give. In contrast, the Hartree–Fock analogue $(1/2)(\rho_\gamma(x)\rho_\gamma(y) - |\gamma(x, y)|^2)$ would give an integral which is too large (unless γ is a projection).
- (5) The prize to be paid for the correct integral condition is that the expression $(1/2)(\rho_\gamma(x)\rho_\gamma(y) - |\gamma^{1/2}(x, y)|^2)$ is, in general, not non-negative (while the true two-particle density and $(1/2)(\rho_\gamma(x)\rho_\gamma(y) - |\gamma(x, y)|^2)$ are). Because of this, the ‘multiplication by $|x|$ ’ strategy [6] to show the existence of a maximum number of electrons seems not to work. As we have already mentioned, we can nevertheless prove this conjecture, based on an alternative argument.
- (6) The ground state energies for neutral atoms (i.e., $N = Z$) in Müller and Hartree–Fock theory agree to within $o(Z^{5/3})$; see [12]. In particular, Müller theory correctly reproduces the Scott and the Dirac–Schwinger corrections to Thomas–Fermi theory.

Convention. Throughout the paper we will assume that $E_Z^M(N)$ has a minimizer γ_0 for some $N \geq Z$. We will write $\rho_0 = \rho_{\gamma_0}$ for short. We will also often write \mathcal{E}^M instead of \mathcal{E}_Z^M .

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2. LOCALIZING DENSITY MATRICES

In this section we collect some known results that will be needed later.

Lemma 4. *For all functions $\chi : \mathbb{R}^3 \rightarrow [-1, 1]$ and all density matrices $0 \leq \gamma \leq 1$, we have*

$$X(\chi\gamma^{1/2}\chi) \leq X((\chi\gamma\chi)^{1/2}) \quad (3)$$

and

$$X(\chi\gamma^{1/2}) \leq \left(\text{Tr}(-\Delta\chi\gamma\chi) \right)^{1/2} \left(\int \chi^2 \rho_\gamma \right)^{1/2} \quad (4)$$

Proof. The first estimate is taken from [2, Lemma 3]. The second estimate follows from the Schwarz and Hardy inequalities:

$$\begin{aligned} X(\chi\gamma^{1/2}) &= \frac{1}{2} \iint \frac{|\chi(x)\gamma^{1/2}(x, y)|^2}{|x - y|} dx dy \\ &\leq \frac{1}{2} \left(\iint \frac{|\chi(x)\gamma^{1/2}(x, y)|^2}{|x - y|^2} dx dy \right)^{1/2} \left(\iint |\chi(x)\gamma^{1/2}(x, y)|^2 dx dy \right)^{1/2} \\ &\leq \left(\text{Tr}(-\Delta\chi\gamma\chi) \right)^{1/2} \left(\int \chi^2 \rho_\gamma \right)^{1/2}. \quad \square \end{aligned}$$

Using this lemma we obtain some rough a-priori bounds for a minimizer γ_0 .

Corollary 5. *If γ_0 is a Müller minimizer, then*

$$\int \rho_0^{5/3} + \text{Tr}(-\Delta\gamma_0) + D(\gamma_0) \leq C \left(Z^{7/3} + N \right) \quad (5)$$

and

$$X(\gamma_0^{1/2}) \leq C \left(Z^{7/3} + N \right)^{1/2} N^{1/2}. \quad (6)$$

Proof. We know from [2, Lemma 1] that $\mathcal{E}_Z^M(\gamma_0) \leq 0$. On the other hand, we deduce from (4) that

$$X(\gamma_0^{1/2}) \leq \left(\text{Tr}(-\Delta\gamma_0) \right)^{1/2} N^{1/2}. \quad (7)$$

and therefore, by the kinetic Lieb–Thirring inequality [8] and the fact that the ground state energy in Thomas–Fermi theory equals a negative constant times $Z^{7/3}$,

$$\begin{aligned} \mathcal{E}_Z^M(\gamma_0) &\geq \frac{1}{4} \text{Tr}(-\Delta\gamma_0) + C^{-1} \int \rho_0^{5/3} - Z \int |x|^{-1} \rho_0 + D(\rho_0) - CN \\ &\geq \frac{1}{4} \text{Tr}(-\Delta\gamma_0) + (2C)^{-1} \int \rho_0^{5/3} + (1/2)D(\rho_0) - CZ^{-7/3} - CN. \end{aligned}$$

This proves (5), and then (6) follows from (7). \square

We next discuss how to localize the Müller energy.

Lemma 6 (IMS-type formula). *For all quadratic partitions of unity $\sum_{i=1}^n f_i^2 = 1$ with $\nabla f_i \in L^\infty$ and for all density matrices $0 \leq \gamma \leq 1$ with $\text{Tr}((1-\Delta)\gamma) < \infty$, we have*

$$\begin{aligned} \sum_{i=1}^n \mathcal{E}_Z^M(f_i \gamma f_i) - \mathcal{E}_Z^M(\gamma) &\leq \int \left(\sum_{i=1}^n |\nabla f_i(x)|^2 \right) \rho_\gamma(x) \, dx \\ &\quad + \sum_{i < j} \iint \frac{f_i(x)^2 \left(|\gamma^{1/2}(x, y)|^2 - \rho_\gamma(x) \rho_\gamma(y) \right) f_j(y)^2}{|x - y|} \, dx \, dy. \end{aligned}$$

Proof. First, for the kinetic term, by the IMS formula,

$$\sum_{i=1}^n \text{Tr}(-\Delta f_i \gamma f_i) - \text{Tr}(-\Delta \gamma) = \text{Tr} \left(\left(\sum_{i=1}^n |\nabla f_i|^2 \right) \gamma \right) = \int \left(\sum_{i=1}^n |\nabla f_i|^2 \right) \rho_\gamma.$$

Next, for the direct term, we also have the exact identity

$$\sum_{i=1}^n D(\rho_{f_i \gamma f_i}) = \sum_{i=1}^n D(f_i^2 \rho_\gamma) = D(\rho_\gamma) - \sum_{i < j} \iint \frac{f_i(x)^2 \rho_\gamma(x) \rho_\gamma(y) f_j(y)^2}{|x - y|} \, dx \, dy.$$

For the correlation-exchange terms, using (3) we can estimate

$$\begin{aligned} - \sum_{i=1}^n X((f_i \gamma f_i)^{1/2}) &\leq - \sum_{i=1}^n X(f_i \gamma^{1/2} f_i) \\ &= -X(\gamma^{1/2}) + \sum_{i < j} \iint \frac{f_i^2(x) |\gamma^{1/2}(x, y)|^2 f_j^2(y)}{|x - y|} \, dx \, dy. \end{aligned}$$

This finishes the proof. \square

3. EXTERIOR L^1 -ESTIMATE

In this section we control $\int_{|x| > r} \rho_0$. We introduce the screened nuclear potential

$$\Phi_r(x) = \frac{Z}{|x|} - \int_{|y| < r} \frac{\rho_0(y)}{|x - y|} \, dy.$$

As was shown in [2], the Müller functional is convex and thus any minimizing density is spherically symmetric. Therefore, when $|x| \geq r$, we may write $\Phi_r(x) = Z_r/|x|$ with $Z_r = Z - \int_{|y| < r} \rho_0(y) \, dy$. As we mentioned in the introduction, the spherical symmetry is not essential for our strategy.

In the rest of the paper, we will use the cut-off function

$$\chi_r^+(x) = \mathbb{1}(|x| \geq r)$$

and a smooth function $\eta_r : \mathbb{R}^3 \rightarrow [0, 1]$ satisfying

$$\chi_r^+ \geq \eta_r \geq \chi_{(1+\lambda)r}^+, \quad |\nabla \eta_r| \leq C(\lambda r)^{-1}. \quad (8)$$

Lemma 7. *For all $r > 0, s > 0, \lambda \in (0, 1/2]$ we have*

$$\begin{aligned} \int \chi_r^+ \rho_0 &\leq C \int_{r < |x| < (1+\lambda)^2 r} \rho_0 + C \left(\sup_{|z| \geq r} [|z| \Phi_r(z)]_+ + s + \lambda^{-2} s^{-1} + \lambda^{-1} \right) \\ &\quad + C \left(s^2 \operatorname{Tr}(-\Delta \eta_r \gamma_0 \eta_r) \right)^{3/5} + C \left(s^2 \operatorname{Tr}(-\Delta \eta_r \gamma_0 \eta_r) \right)^{1/3}. \end{aligned}$$

Proof. From the minimality of γ_0 , we have the binding inequality

$$\mathcal{E}_Z^M(\gamma_0) \leq \mathcal{E}_Z^M(\chi_1 \gamma_0 \chi_1) + \mathcal{E}_{Z=0}^M(\chi_2 \gamma_0 \chi_2) \quad (9)$$

for every partition of unity $\chi_1^2 + \chi_2^2 = 1$. For fixed $\lambda \in (0, 1/2]$, $s > 0, \ell > 0, \nu \in \mathbb{S}^2$ we choose

$$\chi_1(x) = g_1\left(\frac{\nu \cdot \theta(x) - \ell}{s}\right), \quad \chi_2(x) = g_2\left(\frac{\nu \cdot \theta(x) - \ell}{s}\right)$$

where $g_1, g_2 : \mathbb{R} \rightarrow \mathbb{R}$ and $\theta : \mathbb{R}^3 \rightarrow \mathbb{R}^3$ satisfy

$$\begin{aligned} g_1^2 + g_2^2 &= 1, \quad g_1(t) = 1 \text{ if } t \leq 0, \quad g_1(t) = 0 \text{ if } t \geq 1, \quad |\nabla g_1| + |\nabla g_2| \leq C, \\ |\theta(x)| &\leq |x|, \quad \theta(x) = 0 \text{ if } |x| \leq r, \quad \theta(x) = x \text{ if } |x| \geq (1+\lambda)r, \quad |\nabla \theta| \leq C\lambda^{-1}. \end{aligned}$$

Now let us bound the left side of (9) from above. By the IMS-type formula in Lemma 6,

$$\begin{aligned} &\mathcal{E}_Z^M(\chi_1 \gamma_0 \chi_1) + \mathcal{E}_{Z=0}^M(\chi_2 \gamma_0 \chi_2) - \mathcal{E}_Z^M(\gamma_0) \\ &\leq \int (|\nabla \chi_1|^2 + |\nabla \chi_2|^2) \rho_0 + \int \frac{Z \chi_2^2(x) \rho_0(x)}{|x|} dx \\ &\quad + \iint \frac{\chi_2^2(x) (|\gamma_0^{1/2}(x, y)|^2 - \rho_0(x) \rho_0(y)) \chi_1^2(y)}{|x - y|} dx dy. \end{aligned}$$

We have

$$\int (|\nabla \chi_1|^2 + |\nabla \chi_2|^2) \rho_0 \leq C(1 + (\lambda s)^{-2}) \int_{\nu \cdot \theta(x) - s \leq \ell \leq \nu \cdot \theta(x)} \rho_0(x) dx.$$

For the attraction and direct terms, we can estimate

$$\begin{aligned} &\int \frac{Z \chi_2^2(x) \rho_0(x)}{|x|} dx - \iint \frac{\chi_2^2(x) \rho_0(x) \chi_1^2(y) \rho_0(y)}{|x - y|} dx dy \\ &= \int \chi_2^2(x) \rho_0(x) \Phi_r(x) dx - \iint_{|y| \geq r} \frac{\chi_2^2(x) \rho_0(x) \chi_1^2(y) \rho_0(y)}{|x - y|} dx dy \\ &\leq \int_{\ell \leq \nu \cdot \theta(x)} \rho_0(x) [\Phi_r(x)]_+ dx - \iint_{|y| \geq r, \nu \cdot \theta(y) \leq \ell \leq \nu \cdot \theta(x) - s} \frac{\rho_0(x) \rho_0(y)}{|x - y|} dx dy. \end{aligned}$$

Since $\theta(x) = x$ when $|x| \geq (1 + \lambda)r$, we obtain

$$\iint_{\substack{|y| \geq r \\ \nu \cdot \theta(y) \leq \ell \leq \nu \cdot \theta(x) - s}} \frac{\rho_0(x) \rho_0(y)}{|x - y|} dx dy \geq \iint_{\substack{|x|, |y| \geq (1+\lambda)r \\ \nu \cdot y \leq \ell \leq \nu \cdot x - s}} \frac{\rho_0(x) \rho_0(y)}{|x - y|} dx dy.$$

For the correlation-exchange term, we use

$$\iint \frac{\chi_2^2(x) |\gamma_0^{1/2}(x, y)|^2 \chi_1^2(y)}{|x - y|} dx dy \leq \iint_{\nu \cdot \theta(y) - s \leq \ell \leq \nu \cdot \theta(x)} \frac{|\gamma^{1/2}(x, y)|^2}{|x - y|} dx dy.$$

Thus in summary, from (9) it follows that

$$\begin{aligned} & \iint_{\substack{|x|, |y| \geq (1+\lambda)r \\ \nu \cdot y \leq \ell \leq \nu \cdot x - s}} \frac{\rho_0(x)\rho_0(y)}{|x-y|} dx dy \leq C(1 + (\lambda s)^{-2}) \int_{\nu \cdot \theta(x) - s \leq \ell \leq \nu \cdot \theta(x)} \rho_0(x) dx \\ & + \int_{\ell \leq x \cdot \theta(x)} \rho_0(x) [\Phi_r(x)]_+ dx + \iint_{\nu \cdot \theta(y) - s \leq \ell \leq \nu \cdot \theta(x)} \frac{|\gamma^{1/2}(x, y)|^2}{|x-y|} dx dy \quad (10) \end{aligned}$$

for all $s > 0, \ell > 0$ and $\nu \in \mathbb{S}^2$.

Next, we integrate (10) over $\ell \in (0, \infty)$, then average over $\nu \in \mathbb{S}^2$ and use

$$\int_{\mathbb{S}^2} [\nu \cdot z]_+ \frac{d\nu}{4\pi} = \frac{|z|}{4}, \quad \forall z \in \mathbb{R}^3.$$

For the left side, we also use Fubini's theorem and

$$\int_0^\infty \left(\mathbf{1}(b \leq \ell \leq a - s) + \mathbf{1}(-a \leq \ell \leq -b - s) \right) d\ell \geq [a - b]_+ - 2s$$

with $a = \nu \cdot x, b = \nu \cdot y$. For the right side, we use the fact that $\{x : \nu \cdot \theta(x) \geq \ell\} \subset \{x : |x| \geq r\}$ since $\ell > 0$ and $\theta(x) = 0$ when $|x| < r$. All this leads to

$$\begin{aligned} & \frac{1}{2} \iint_{|x|, |y| \geq (1+\lambda)r} \frac{|x-y|/4 - 2s}{|x-y|} \rho_0(x)\rho_0(y) dx dy \\ & \leq C(s + \lambda^{-2}s^{-1}) \int_{|x| \geq r} \rho_0(x) dx + \int_{|x| \geq r} [|\theta(x)|/4] [\Phi_r(x)]_+ \rho_0(x) dx \\ & + \iint_{|x| \geq r} \frac{|\theta(x) - \theta(y)|/4 + s}{|x-y|} |\gamma^{1/2}(x, y)|^2 dx dy. \end{aligned}$$

Using $|\theta(x)| \leq |x|$ and $|\theta(x) - \theta(y)| \leq C\lambda^{-1}|x-y|$, we can simplify the above estimate to

$$\begin{aligned} \frac{1}{8} \left(\int \chi_{(1+\lambda)r}^+ \rho_0 \right)^2 & \leq \left(\frac{1}{4} \sup_{|z| \geq r} [z|\Phi_r(z)]_+ + Cs + C\lambda^{-2}s^{-1} + C\lambda^{-1} \right) \int \chi_r^+ \rho_0 \\ & + sD(\chi_{(1+\lambda)r}^+ \rho_0) + s \iint \frac{\chi_r^+(x) |\gamma^{1/2}(x, y)|^2}{|x-y|} dx dy. \end{aligned}$$

In order to bring this estimate in the desired form, let us replace r by $(1+\lambda)r$ in the latter inequality and write

$$\begin{aligned} & \frac{1}{8} \left(\int \chi_{(1+\lambda)^2r}^+ \rho_0 \right)^2 \\ & \leq \left(\frac{1}{4} \sup_{|z| \geq (1+\lambda)r} [z|\Phi_{(1+\lambda)r}(z)]_+ + Cs + C\lambda^{-2}s^{-1} + C\lambda^{-1} \right) \int \chi_{(1+\lambda)r}^+ \rho_0 \\ & + sD(\chi_{(1+\lambda)^2r}^+ \rho_0) + s \iint \frac{\chi_{(1+\lambda)r}^+(x) |\gamma^{1/2}(x, y)|^2}{|x-y|} dx dy. \quad (11) \end{aligned}$$

We can estimate the left side of (11) as

$$\left(\int \chi_{(1+\lambda)^2r}^+ \rho_0 \right)^2 \geq \frac{1}{2} \left(\int \chi_r^+ \rho_0 \right)^2 - \left(\int_{r < |x| < (1+\lambda)^2r} \rho_0 \right)^2.$$

Now we estimate the right side of (11). For the first term, we can simply use $\Phi_{(1+\lambda)r}(z) \leq \Phi_r(z)$ and $\chi_{(1+\lambda)r} \leq \chi_r$ to get

$$\begin{aligned} & \left(\frac{1}{4} \sup_{|z| \geq (1+\lambda)r} [|z| \Phi_{(1+\lambda)r}(z)]_+ + Cs + C\lambda^{-2}s^{-1} + C\lambda^{-1} \right) \int \chi_{(1+\lambda)r}^+ \rho_0 \\ & \leq \left(\frac{1}{4} \sup_{|z| \geq r} [|z| \Phi_r(z)]_+ + Cs + C\lambda^{-2}s^{-1} + C\lambda^{-1} \right) \int \chi_r^+ \rho_0. \end{aligned}$$

For the second term, by the Hardy–Littewood–Sobolev, Hölder and Lieb–Thirring inequalities,

$$\begin{aligned} D(\chi_{(1+\lambda)^2r}^+ \rho_0) & \leq C \|\chi_{(1+\lambda)^2r}^+ \rho_0\|_{L^{6/5}}^2 \leq C \|\chi_{(1+\lambda)^2r}^+ \rho_0\|_{L^1}^{7/6} \|\chi_{(1+\lambda)^2r}^+ \rho_0\|_{L^{5/3}}^{5/6} \\ & \leq C \|\chi_r^+ \rho_0\|_{L^1}^{7/6} \left(\text{Tr}(-\Delta \eta_r \gamma_0 \eta_r) \right)^{1/2}. \end{aligned}$$

Here we have used $\eta_r^2 \geq \chi_{(1+\lambda)^2r}^+$. For the third term, by (4),

$$\begin{aligned} \iint \frac{\chi_{(1+\lambda)r}^+(x) |\gamma^{1/2}(x, y)|^2}{|x - y|} dx dy & \leq \iint \frac{\eta_r(x)^2 |\gamma^{1/2}(x, y)|^2}{|x - y|} dx dy \\ & \leq 2 \left(\text{Tr}(-\Delta \eta_r \gamma_0 \eta_r) \right)^{1/2} \left(\int \chi_r^+ \rho_0 \right)^{1/2}. \end{aligned}$$

Thus from (11), we deduce that

$$\begin{aligned} \left(\int \chi_r^+ \rho_0 \right)^2 & \leq C \left(\int_{r < |x| < (1+\lambda)^2r} \rho_0 \right)^2 \\ & \quad + C \left(\sup_{|z| \geq r} [|z| \Phi_r(z)]_+ + s + \lambda^{-2}s^{-1} + \lambda^{-1} \right) \int \chi_r^+ \rho_0 \\ & \quad + Cs \left(\chi_r^+ \rho_0 \right)^{7/6} \left(\text{Tr}(-\Delta \eta_r \gamma_0 \eta_r) \right)^{1/2} \\ & \quad + Cs \left(\text{Tr}(-\Delta \eta_r \gamma_0 \eta_r) \right)^{1/2} \left(\int \chi_r^+ \rho_0 \right)^{1/2}. \end{aligned}$$

This implies that

$$\begin{aligned} \int \chi_r^+ \rho_0 & \leq C \int_{r < |x| < (1+\lambda)^2r} \rho_0 + C \left(\sup_{|z| \geq r} [|z| \Phi_r(z)]_+ + s + \lambda^{-2}s^{-1} + \lambda^{-1} \right) \\ & \quad + C \left(s^2 \text{Tr}(-\Delta \eta_r \gamma_0 \eta_r) \right)^{3/5} + C \left(s^2 \text{Tr}(-\Delta \eta_r \gamma_0 \eta_r) \right)^{1/3}. \quad \square \end{aligned}$$

As a by-product of the above proof, we get the following important a-priori bounds.

Corollary 8. *If γ_0 is a Müller minimizer, then*

$$\text{Tr} \gamma_0 = N \leq 2Z + C(Z^{2/3} + 1). \quad (12)$$

Moreover,

$$\int \rho_0^{5/3} + \text{Tr}(-\Delta \gamma_0) + D(\gamma_0) \leq C \left(Z^{7/3} + 1 \right) \quad (13)$$

and

$$X(\gamma_0^{1/2}) \leq C \left(Z^{5/3} + 1 \right). \quad (14)$$

We emphasize that (12) proves the conjecture from [2] that there is a critical electron number.

Proof. In (11), we can choose $\lambda = 1/2$ and take $r \rightarrow 0^+$. This leads to

$$N^2 \leq (2Z + Cs + Cs^{-1} + C)N + CsD(\rho_0) + CsX(\gamma_0^{1/2}).$$

Optimizing over $s > 0$, we deduce that

$$N \leq 2Z + C + C\sqrt{\left(D(\rho_0) + X(\gamma_0^{1/2}) + N\right)N^{-1}} \quad (15)$$

According to the a-priori bounds (5) and (6) we have

$$D(\gamma_0) + X(\gamma_0) \leq C(Z^{7/3} + N).$$

Inserting this bound into (15) we obtain (12). The bounds (13) and (14) now follow immediately from (5) and (6). \square

4. SPLITTING OUTSIDE FROM INSIDE

Recall that we have introduced a smooth cut-off function $\eta_r : \mathbb{R}^3 \rightarrow [0, 1]$ satisfying

$$\chi_r^+ \geq \eta_r \geq \chi_{(1+\lambda)r}^+$$

with $\lambda \in (0, 1/2]$. Of course, we can choose η_r such that there is a quadratic partition of unity

$$\eta_-^2 + \eta_{(0)}^2 + \eta_r^2 = 1$$

with

$$\begin{aligned} \text{supp } \eta_- &\subset \{|x| \leq r\}, \quad \text{supp } \eta_{(0)} \subset \{(1-\lambda)r \leq |x| \leq (1+\lambda)r\}, \\ \eta_-(x) &= 1 \text{ if } |x| \leq (1-\lambda)r, \quad |\nabla \eta_-|^2 + |\nabla \eta_{(0)}|^2 + |\nabla \eta_r|^2 \leq C(\lambda r)^{-2}. \end{aligned}$$

Let us introduce the reduced Hartree-Fock functional

$$\mathcal{E}_r^{\text{RHF}}(\gamma) = \text{Tr}(-\Delta\gamma) - \int \Phi_r(x)\rho_\gamma(x) dx + D(\rho_\gamma). \quad (16)$$

The main result of this section is

Lemma 9. *For all $r > 0$, all $\lambda \in (0, 1/2]$, all density matrices $0 \leq \gamma \leq 1$ satisfying $\text{supp } \rho_\gamma \subset \{x : |x| \geq r\}$ and $\text{Tr } \gamma \leq \int \chi_r^+ \rho_0$ we have*

$$\mathcal{E}_r^{\text{RHF}}(\eta_r \gamma_0 \eta_r) \leq \mathcal{E}_r^{\text{RHF}}(\gamma) + \mathcal{R}$$

where

$$\begin{aligned} \mathcal{R} &\leq C(1 + (\lambda r)^{-2}) \int_{(1-\lambda)r \leq |x| \leq (1+\lambda)r} \rho_0 + C\lambda r^3 \sup_{|z| \geq (1-\lambda)r} [\Phi_{(1-\lambda)r}(z)]_+^{5/2} \\ &\quad + C \left(\text{Tr}(-\Delta \eta_r \gamma_0 \eta_r) \right)^{1/2} \left(\int \eta_r \rho_0 \right)^{1/2}. \end{aligned}$$

Proof. It suffices to show that

$$\mathcal{E}^{\text{M}}(\eta_- \gamma_0 \eta_-) + \mathcal{E}_r^{\text{RHF}}(\eta_r \gamma_0 \eta_r) - \mathcal{R} \leq \mathcal{E}^{\text{M}}(\gamma_0) \leq \mathcal{E}^{\text{M}}(\eta_- \gamma_0 \eta_-) + \mathcal{E}_r^{\text{RHF}}(\gamma) \quad (17)$$

Here and in the following the subscript Z of \mathcal{E}^{M} is dropped for simplicity.

Upper bound. From the minimality of γ_0 and the fact that $N \mapsto E^{\text{M}}(N)$ is non-increasing, we have

$$\mathcal{E}^{\text{M}}(\gamma_0) \leq \mathcal{E}^{\text{M}}(\eta_- \gamma_0 \eta_- + \gamma).$$

Since η_- and ρ_γ have disjoint supports, we have the operator identity

$$(\eta_- \gamma_0 \eta_- + \gamma)^{1/2} = (\eta_- \gamma_0 \eta_-)^{1/2} + \gamma^{1/2}$$

and the kernel identity

$$|(\eta_- \gamma_0 \eta_- + \gamma)^{1/2}(x, y)|^2 = |(\eta_- \gamma_0 \eta_-)^{1/2}(x, y)|^2 + |\gamma^{1/2}(x, y)|^2.$$

Therefore, we can split the exchange term

$$X((\eta_- \gamma_0 \eta_- + \gamma)^{1/2}) = X((\eta_- \gamma_0 \eta_-)^{1/2}) + X(\gamma^{1/2}).$$

Consequently,

$$\begin{aligned} \mathcal{E}^M(\eta_- \gamma_0 \eta_- + \gamma) &= \mathcal{E}^M(\eta_- \gamma_0 \eta_-) + \mathcal{E}^M(\gamma) + \iint \frac{(\eta_-^2 \rho_0)(x) \rho_\gamma(y)}{|x - y|} dx dy \\ &\leq \mathcal{E}^M(\eta_- \gamma_0 \eta_-) + \mathcal{E}_{r=0}^{\text{RHF}}(\gamma) + \iint_{|x| \leq r} \frac{\rho_0(x) \rho_\gamma(y)}{|x - y|} dx dy \\ &= \mathcal{E}^M(\eta_- \gamma_0 \eta_-) + \mathcal{E}_r^{\text{RHF}}(\gamma). \end{aligned}$$

Thus,

$$\mathcal{E}^M(\gamma_0) \leq \mathcal{E}^M(\eta_- \gamma_0 \eta_- + \gamma) \leq \mathcal{E}^M(\eta_- \gamma_0 \eta_-) + \mathcal{E}_r^{\text{RHF}}(\gamma).$$

This is the upper bound in (17).

Lower bound. By the IMS-type formula in Lemma 6,

$$\begin{aligned} \mathcal{E}^M(\gamma_0) &\geq \mathcal{E}^M(\eta_- \gamma_0 \eta_-) + \mathcal{E}^M(\eta_{(0)} \gamma_0 \eta_{(0)}) + \mathcal{E}^M(\eta_r \gamma_0 \eta_r) \\ &\quad - \int \left(|\nabla \eta_-|^2 + |\nabla \eta_{(0)}|^2 + |\nabla \eta_r|^2 \right) \rho_0 \\ &\quad + \iint \frac{\eta_r(x)^2 \rho_0(x) \rho_0(y) (\eta_-(y)^2 + \eta_{(0)}(y))^2}{|x - y|} dx dy \\ &\quad + \iint \frac{\eta_{(0)}(x)^2 \rho_0(x) \rho_0(y) \eta_-(y)^2}{|x - y|} dx dy \\ &\quad - \iint \frac{(\eta_r(x)^2 + \eta_{(0)}(x)^2) |\gamma_0^{1/2}(x, y)|^2}{|x - y|} dx dy. \end{aligned}$$

We have

$$- \int \left(|\nabla \eta_-|^2 + |\nabla \eta_{(0)}|^2 + |\nabla \eta_r|^2 \right) \rho_0 \geq -C(\lambda r)^{-2} \int_{(1-\lambda)r \leq |x| \leq (1+\lambda)r} \rho_0.$$

Moreover,

$$\begin{aligned}
& \mathcal{E}^{\text{M}}(\eta_r \gamma_0 \eta_r) + \iint \frac{\eta_r(x)^2 \rho_0(x) \rho_0(y) (\eta_-(y)^2 + \eta_{(0)}(y))^2}{|x-y|} dx dy \\
& \quad - \iint \frac{\eta_r(x)^2 |\gamma_0^{1/2}(x, y)|^2}{|x-y|} dx dy \\
& \geq \mathcal{E}^{\text{M}}(\eta_r \gamma_0 \eta_r) + \iint_{|y| \leq r} \frac{\eta_r(x)^2 \rho_0(x) \rho_0(y)}{|x-y|} dx dy \\
& \quad - \iint \frac{\eta_r(x)^2 |\gamma_0^{1/2}(x, y)|^2}{|x-y|} dx dy \\
& = \mathcal{E}_r^{\text{RHF}}(\eta_r \gamma_0 \eta_r) - X((\eta_r \gamma_0 \eta_r)^{1/2}) - \iint \frac{\eta_r(x)^2 |\gamma_0^{1/2}(x, y)|^2}{|x-y|} dx dy \\
& \geq \mathcal{E}_r^{\text{RHF}}(\eta_r \gamma_0 \eta_r) - 3 \left(\text{Tr}(-\Delta \eta_r \gamma_0 \eta_r) \right)^{1/2} \left(\int \eta_r^2 \rho_0 \right)^{1/2}.
\end{aligned}$$

In the last inequality we have used (4) twice, once with $\chi = 1$ and once with $\chi = \eta_r$. Similarly, we have

$$\begin{aligned}
& \mathcal{E}^{\text{M}}(\eta_{(0)} \gamma_0 \eta_{(0)}) + \iint \frac{\eta_{(0)}(x)^2 \rho_0(x) \rho_0(y) \eta_-(y)^2}{|x-y|} dx dy \\
& \quad - \iint \frac{\eta_{(0)}(x)^2 |\gamma_0^{1/2}(x, y)|^2}{|x-y|} dx dy \\
& \geq \mathcal{E}^{\text{M}}(\eta_{(0)} \gamma_0 \eta_{(0)}) + \iint_{|y| \leq (1-\lambda)r} \frac{\eta_{(0)}(x)^2 \rho_0(x) \rho_0(y)}{|x-y|} dx dy \\
& \quad - \iint \frac{\eta_{(0)}(x)^2 |\gamma_0^{1/2}(x, y)|^2}{|x-y|} dx dy \\
& = \mathcal{E}_{(1-\lambda)r}^{\text{RHF}}(\eta_{(0)} \gamma_0 \eta_{(0)}) - X((\eta_{(0)} \gamma_0 \eta_{(0)})^{1/2}) - \iint \frac{\eta_{(0)}(x)^2 |\gamma_0^{1/2}(x, y)|^2}{|x-y|} dx dy \\
& \geq \mathcal{E}_{(1-\lambda)r}^{\text{RHF}}(\eta_{(0)} \gamma_0 \eta_{(0)}) - 3 \left(\text{Tr}(-\Delta \eta_{(0)} \gamma_0 \eta_{(0)}) \right)^{1/2} \left(\int \eta_{(0)}^2 \rho_0 \right)^{1/2} \\
& \geq \text{Tr}((-(1/2)\Delta - \Phi_{(1-\lambda)r}) \eta_{(0)} \gamma_0 \eta_{(0)}) - C \int \eta_{(0)}^2 \rho_0. \tag{18}
\end{aligned}$$

Applying the Lieb–Thirring inequality with $V = \Phi_{(1-\lambda)r} \mathbf{1}_{\text{supp } \eta_{(0)}}$, we obtain

$$\begin{aligned}
\text{Tr}((-(1/2)\Delta - \Phi_{(1-\lambda)r}) \eta_{(0)} \gamma_0 \eta_{(0)}) & \geq \text{Tr}[-(1/2)\Delta - V]_- \geq -C \int V^{5/2} \\
& \geq -C \lambda r^3 \sup_{|x| \geq (1-\lambda)r} [\Phi_{(1-\lambda)r}(x)]_+^{5/2}.
\end{aligned}$$

Thus (18) implies that

$$\begin{aligned} & \mathcal{E}^M(\eta_{(0)}\gamma_0\eta_{(0)}) + \iint \frac{\eta_{(0)}(x)^2\rho_0(x)\rho_0(y)\eta_{-}(y)^2}{|x-y|} dx dy \\ & - \iint \frac{\eta_{(0)}(x)^2|\gamma_0^{1/2}(x,y)|^2}{|x-y|} dx dy \\ & \geq -C\lambda r^3 \sup_{|x|\geq(1-\lambda)r} [\Phi_{(1-\lambda)r}(x)]_+^{5/2} - C \int_{(1-\lambda)r\leq|x|\leq(1+\lambda)r} \rho_0. \end{aligned}$$

Putting everything together, we conclude that

$$\begin{aligned} \mathcal{E}^M(\gamma_0) & \geq \mathcal{E}^M(\eta_{-}\gamma_0\eta_{-}) + \mathcal{E}_r^{\text{RHF}}(\eta_r\gamma_0\eta_r) \\ & - C(1+(\lambda r)^{-2}) \int_{(1-\lambda)r\leq|x|\leq(1+\lambda)r} \rho_0 \\ & - C\lambda r^3 \sup_{|x|\geq(1-\lambda)r} [\Phi_{(1-\lambda)r}(x)]_+^{5/2} \\ & - 3 \left(\text{Tr}(-\Delta\eta_r\gamma_0\eta_r) \right)^{1/2} \left(\int \eta_r\rho_0 \right)^{1/2}. \end{aligned}$$

This implies the lower bound in (17). \square

As a by-product of the above proof we obtain

Lemma 10. *For all $r > 0$ and all $\lambda \in (0, 1/2]$ we have*

$$\begin{aligned} \text{Tr}(-\Delta\eta_r\gamma_0\eta_r) & \leq C(1+(\lambda r)^{-2}) \int \chi_{(1-\lambda)r}^+ \rho_0 \\ & + C\lambda r^3 \sup_{|z|\geq(1-\lambda)r} [\Phi_{(1-\lambda)r}(z)]_+^{5/2} + C \sup_{|z|\geq r} [|z|\Phi_r(z)]_+^{7/3}. \end{aligned}$$

Proof. We apply Lemma 9 with $\gamma = 0$ and obtain $\mathcal{E}_r^{\text{RHF}}(\eta_r\gamma_0\eta_r) \leq \mathcal{R}$. On the other hand, by the kinetic Lieb–Thirring inequality and the fact that the ground state energy in Thomas–Fermi theory is a negative constant times $-Z^{7/3}$, we have

$$\begin{aligned} \mathcal{E}_r^{\text{RHF}}(\eta_r\gamma_0\eta_r) & \geq (1/2) \text{Tr}(-\Delta\eta_r\gamma_0\eta_r) \\ & + C^{-1} \int (\eta_r^2\rho_0)^{5/3} - \sup_{|z|\geq r} [|z|\Phi_r(z)]_+ \int \frac{\eta_r^2\rho_0}{|x|} + D(\eta_r^2\rho_0) \\ & = (1/2) \text{Tr}(-\Delta\eta_r\gamma_0\eta_r) - C \sup_{|z|\geq r} [|z|\Phi_r(z)]_+^{7/3}. \end{aligned}$$

Therefore,

$$\text{Tr}(-\Delta\eta_r\gamma_0\eta_r) \leq C\mathcal{R} + C \sup_{|z|\geq r} [|z|\Phi_r(z)]_+^{7/3},$$

which implies the lemma. \square

5. A COLLECTION OF USEFUL FACTS

5.1. Semiclassical analysis. In order to compare Müller theory with Thomas–Fermi theory, we use a semiclassical approximation. The following

results are taken from [15, Lemma 8.2] (more precisely, we have optimized over $\delta > 0$ and changed $V \mapsto 2V$). We put

$$L_{\text{sc}} = (15\pi^2)^{-1}.$$

Lemma 11. *For $s > 0$, fix a smooth function $g : \mathbb{R}^3 \rightarrow [0, 1]$ such that*

$$\text{supp } g \subset \{|x| \leq s\}, \quad \int g^2 = 1, \quad \int |\nabla g|^2 \leq Cs^{-2}.$$

(i) *For all $V : \mathbb{R}^3 \rightarrow \mathbb{R}$ such that $[V]_+, [V - V * g^2]_+ \in L^{5/2}$ and for all density matrices $0 \leq \gamma \leq 1$, we have*

$$\begin{aligned} \text{Tr}((-\Delta - V)\gamma) &\geq -L_{\text{sc}} \int [V]_+^{5/2} - Cs^{-2} \text{Tr } \gamma \\ &\quad - C \left(\int [V]_+^{5/2} \right)^{3/5} \left(\int [V - V * g^2]_+^{5/2} \right)^{2/5}. \end{aligned} \quad (19)$$

(ii) *On the other hand, if $[V]_+ \in L^{5/2} \cap L^{3/2}$, then there is a density matrix γ such that*

$$\rho_\gamma = \frac{5}{2} L_{\text{sc}} [V]_+^{3/2} * g^2$$

and

$$\text{Tr}(-\Delta\gamma) \leq \frac{3}{2} L_{\text{sc}} \int [V]_+^{5/2} + Cs^{-2} \int [V]_+^{3/2}. \quad (20)$$

5.2. Coulomb potential estimate. The following bound is essentially contained in [15, Cor. 9.3] and appears explicitly in [4, Lem. 18] (applied to both $\pm f$).

Lemma 12. *For every $f \in L^{5/3} \cap L^{6/5}(\mathbb{R}^3)$ and $x \in \mathbb{R}^3$, we have*

$$\left| \int_{|y| < |x|} \frac{f(y)}{|x - y|} dy \right| \leq C \|f\|_{L^{5/3}}^{5/6} (|x| D(f))^{1/12}. \quad (21)$$

6. SCREENED POTENTIAL ESTIMATE

From now on we always assume that γ_0 is a minimizer for $E_Z^{\text{M}}(N)$ with $N \geq Z \geq 1$. Our main tool to prove the ionization bound is the following

Lemma 13 (Screened potential estimate). *There are universal constants $C > 0, \varepsilon > 0, D > 0$ such that*

$$|\Phi_{|x|}(x) - \Phi_{|x|}^{\text{TF}}(x)| \leq C|x|^{-4+\varepsilon}, \quad \forall |x| \leq D.$$

We prove Lemma 13 using a bootstrap argument based on two lemmas.

Lemma 14 (Initial step). *There is a universal constant $C_1 > 0$ such that*

$$|\Phi_{|x|}(x) - \Phi_{|x|}^{\text{TF}}(x)| \leq C_1 Z^{49/36-a} |x|^{1/12}, \quad \forall |x| > 0,$$

with $a = 1/198$.

Lemma 15 (Iterative step). *There are universal constants $C_2, \beta, \delta, \varepsilon > 0$ such that, if*

$$|\Phi_{|x|}(x) - \Phi_{|x|}^{\text{TF}}(x)| \leq \beta |x|^{-4}, \quad \forall |x| \leq D \quad (22)$$

for some $D \in [Z^{-1/3}, 1]$, then

$$|\Phi_{|x|}(x) - \Phi_{|x|}^{\text{TF}}(x)| \leq C_2 |x|^{-4+\varepsilon}, \quad \forall D \leq |x| \leq D^{1-\delta}. \quad (23)$$

Let us prove Lemma 13 using Lemmas 14 and 15. The proof is identical to [4, Proof of Lemma 15], but is repeated here for the convenience of the reader.

Proof of Lemma 13. We use the notations in Lemmas 14 and 15 and set $\sigma = \max\{C_1, C_2\}$. Without loss of generality we may assume that $\beta < \sigma$ and $\varepsilon \leq 3a = 1/66$. Let us denote

$$D_n = Z^{-\frac{1}{3}(1-\delta)^n}, \quad n = 0, 1, 2, \dots$$

From Lemma 14, we have

$$|\Phi_{|x|}(x) - \Phi_{|x|}^{\text{TF}}(x)| \leq C_1 Z^{49/36-a} |x|^{1/12} \leq \sigma |x|^{-4+\varepsilon}, \quad \forall |x| \leq D_0 = Z^{-1/3}.$$

From Lemma 15, we deduce by induction that for all $n = 0, 1, 2, \dots$, if

$$\sigma(D_n)^\varepsilon \leq \beta,$$

then

$$|\Phi_{|x|}(x) - \Phi_{|x|}^{\text{TF}}(x)| \leq \sigma |x|^{-4+\varepsilon}, \quad \forall |x| \leq D_{n+1}.$$

Note that $D_n \rightarrow 1$ as $n \rightarrow \infty$ and that $\sigma > \beta$. Thus, there is a minimal $n_0 = 0, 1, 2, \dots$ such that $\sigma(D_{n_0})^\varepsilon > \beta$. If $n_0 \geq 1$, then $\sigma(D_{n_0-1})^\varepsilon \leq \beta$ and therefore by the preceding argument

$$|\Phi_{|x|}(x) - \Phi_{|x|}^{\text{TF}}(x)| \leq \sigma |x|^{-4+\varepsilon}, \quad \forall |x| \leq D_{n_0}.$$

As we have already shown, the same bound holds for $n_0 = 0$. Let $D = (\sigma^{-1}\beta)^{1/\varepsilon}$, which is a universal constant, and note that by choice of n_0 we have $D_{n_0} \geq D$. \square

We will prove Lemmas 14 and 15 in the following two sections.

7. INITIAL STEP

In this section we prove Lemma 14. Recall that we always assume $Z \geq 1$. For simplicity we write

$$\mathcal{E}^{\text{RHF}}(\gamma) = \mathcal{E}_{r=0}^{\text{RHF}}(\gamma) = \text{Tr}(-\Delta\gamma) - \int_{\mathbb{R}^3} \frac{Z\rho_\gamma(x)}{|x|} dx + D(\rho_\gamma).$$

Proof of Lemma 14. The strategy is to bound $\mathcal{E}^{\text{M}}(\gamma_0)$ from above and below using the semi-classical estimates from Lemma 11. The main term in both bounds is $\mathcal{E}^{\text{TF}}(\rho^{\text{TF}})$, but in the lower bound we will get an additional term $D(\rho_0 - \rho^{\text{TF}})$. The error terms in the upper and lower bounds will then give an upper bound on $D(\rho_0 - \rho^{\text{TF}})$ which will imply the lemma.

Upper bound. We shall show that

$$\mathcal{E}^{\text{M}}(\gamma_0) \leq \mathcal{E}^{\text{TF}}(\rho^{\text{TF}}) + CZ^{11/5}. \quad (24)$$

Indeed, since

$$N \mapsto \inf\{\mathcal{E}_Z^{\text{M}}(\gamma) \mid 0 \leq \gamma \leq 1, \text{Tr } \gamma = N\}$$

is non-increasing (indeed, it is even non-increasing when $N/16$ is added, see [2, Proposition 4] and note the different convention for the kinetic energy)

and since the contribution of the exchange term to the energy is non-positive, we have

$$\begin{aligned}\mathcal{E}^{\text{M}}(\gamma_0) &\leq \inf\{\mathcal{E}_Z^{\text{M}}(\gamma) \mid 0 \leq \gamma \leq 1, \text{Tr } \gamma \leq N\} \\ &\leq \inf\{\mathcal{E}^{\text{RHF}}(\gamma) \mid 0 \leq \gamma \leq 1, \text{Tr } \gamma \leq N\}.\end{aligned}\quad (25)$$

Thus, (24) follows from a well-known bound on the ground state energy in reduced Hartree–Fock theory (essentially in [5, Proof of Theorem 5.1]), but we include a proof for the sake of completeness. We introduce the Thomas–Fermi potential

$$\varphi^{\text{TF}}(x) = \frac{Z}{|x|} - \rho^{\text{TF}} * |x|^{-1}$$

and apply Lemma 11 (ii) with $V = \varphi^{\text{TF}}$ and a spherically symmetric g to obtain a density matrix γ' . Because of the Thomas–Fermi equation we have

$$\rho_{\gamma'} = \frac{5}{2}L_{\text{sc}}(\varphi^{\text{TF}})^{3/2} * g^2 = \rho^{\text{TF}} * g^2.$$

Since

$$\text{Tr } \gamma' = \int \rho_{\gamma'} = \int \rho^{\text{TF}} = Z \leq N,$$

we obtain

$$\inf\{\mathcal{E}^{\text{RHF}}(\gamma) \mid 0 \leq \gamma \leq 1, \text{Tr } \gamma \leq N\} \leq \mathcal{E}^{\text{RHF}}(\gamma').$$

By the semiclassical estimate from Lemma 11 (ii)

$$\begin{aligned}\mathcal{E}^{\text{RHF}}(\gamma') &\leq \frac{3}{2}L_{\text{sc}} \int [V]_+^{5/2} + Cs^{-2} \int [V]_+^{3/2} - \int \frac{Z}{|x|} (\rho^{\text{TF}} * g^2) \\ &\quad + D(\rho^{\text{TF}} * g^2) \\ &\leq c^{\text{TF}} \int [\rho^{\text{TF}}]_+^{5/3} - \int \frac{Z}{|x|} \rho^{\text{TF}} + D(\rho^{\text{TF}}) \\ &\quad + Cs^{-2} \int \rho^{\text{TF}} + \int \left(\frac{Z}{|x|} - \frac{Z}{|x|} * g^2 \right) \rho^{\text{TF}} \\ &= \mathcal{E}^{\text{TF}}(\rho^{\text{TF}}) + Cs^{-2} \int \rho^{\text{TF}} + \int \left(\frac{Z}{|x|} - \frac{Z}{|x|} * g^2 \right) \rho^{\text{TF}},\end{aligned}$$

where we have used the convexity of D in the second inequality. By Newton's theorem, $|x|^{-1} - |x|^{-1} * g^2$ is non-negative, bounded by $|x|^{-1}$ and vanishes when $|x| > s$. Moreover, bounding φ^{TF} in the Thomas–Fermi equation from above by $Z|x|^{-1}$, we find

$$\rho^{\text{TF}}(x) \leq \left(\frac{3}{5c^{\text{TF}}} \right)^{3/2} Z^{3/2} |x|^{-3/2}.$$

These facts yield

$$\int \left(\frac{Z}{|x|} - \frac{Z}{|x|} * g^2 \right) \rho^{\text{TF}} \leq CZ^{5/2} s^{1/2}.$$

Thus, after optimization in s ,

$$\mathcal{E}^{\text{RHF}}(\gamma') \leq \mathcal{E}^{\text{TF}}(\rho^{\text{TF}}) + CZ^{11/5}.$$

Combining this with (25) we obtain (24).

Lower bound. We now show that

$$\mathcal{E}^M(\gamma_0) \geq \mathcal{E}^{\text{TF}}(\rho^{\text{TF}}) + D(\rho_0 - \rho^{\text{TF}}) - CZ^{25/11}. \quad (26)$$

With the Thomas–Fermi potential introduced above we can write

$$\mathcal{E}^M(\gamma_0) = \text{Tr}((-\Delta - \varphi^{\text{TF}})\gamma_0) + D(\rho_0 - \rho^{\text{TF}}) - D(\rho^{\text{TF}}) - X(\gamma_0^{1/2}).$$

According to (14) we can bound the exchange term by

$$X(\gamma_0^{1/2}) \leq CZ^{5/3}.$$

Next, from the semiclassical estimate (19) we have

$$\begin{aligned} \text{Tr}((-\Delta - \varphi^{\text{TF}})\gamma_0) &\geq -L_{\text{sc}} \int [\varphi^{\text{TF}}]_+^{5/2} - Cs^{-2} \text{Tr} \gamma_0 \\ &\quad - C \left(\int [\varphi^{\text{TF}}]_+^{5/2} \right)^{3/5} \left(\int [\varphi^{\text{TF}} - \varphi^{\text{TF}} * g^2]_+^{5/2} \right)^{2/5}. \end{aligned}$$

According to (12) we can bound $\text{Tr} \gamma_0 = N \leq CZ$. Moreover, by scaling,

$$\int |\varphi^{\text{TF}}|^{5/2} = C \int (\rho^{\text{TF}})^{5/3} \leq CZ^{7/3}$$

and, as explained in [15, end of page 554],

$$\int |\varphi^{\text{TF}} - \varphi^{\text{TF}} * g^2|^{5/2} \leq CZ^{5/2} s^{1/2}.$$

Thus,

$$\text{Tr}((-\Delta - \varphi^{\text{TF}})\gamma_0) \geq -L_{\text{sc}} \int [\varphi^{\text{TF}}]_+^{5/2} - Cs^{-2}Z - CZ^{12/5}s^{1/5}.$$

Optimizing over $s > 0$ we get

$$\text{Tr}((-\Delta - \varphi^{\text{TF}})\gamma_0) \geq -L_{\text{sc}} \int [\varphi^{\text{TF}}]_+^{5/2} - CZ^{25/11}.$$

Note that from the Thomas–Fermi equation, we have

$$-L_{\text{sc}} \int [\varphi^{\text{TF}}]_+^{5/2} - D(\rho^{\text{TF}}) = \mathcal{E}^{\text{TF}}(\rho^{\text{TF}}), \quad (27)$$

which proves (26).

Conclusion. Combining (24) and (26) we infer that

$$D(\rho_0 - \rho^{\text{TF}}) \leq CZ^{25/11}.$$

From the Coulomb estimate (21) with $f = \rho_0 - \rho^{\text{TF}}$ and the kinetic estimates

$$\int \rho_0^{5/3} \leq CZ^{7/3}, \quad \int (\rho^{\text{TF}})^{5/3} \leq CZ^{7/3},$$

(the first one follows from (13) and the second one follows simply by scaling) we find that for all $|x| > 0$,

$$\begin{aligned} |\Phi_{|x|}(x) - \Phi_{|x|}^{\text{TF}}(x)| &= \left| \int_{|y| < |x|} \frac{\rho_0(y) - \rho^{\text{TF}}(y)}{|x - y|} dy \right| \\ &\leq C \|\rho_0 - \rho^{\text{TF}}\|_{L^{5/3}}^{5/6} (|x| D(\rho_0 - \rho^{\text{TF}}))^{1/12} \\ &\leq CZ^{179/132} |x|^{1/12}. \end{aligned}$$

Since $179/132 = 49/36 - 1/198$, this is the desired bound. \square

8. ITERATIVE STEP

In this section we will prove Lemma 15. We split the proof into five steps.

Step 1. We collect some easy consequences of (22).

Lemma 16. *Assume that (22) holds true for some $\beta, D \in (0, 1]$. Then for all $r \in (0, D]$, we have*

$$\left| \int_{|x|<r} (\rho_0 - \rho^{\text{TF}}) \right| \leq \beta r^{-3}, \quad (28)$$

$$\sup_{|x| \geq r} |x| |\Phi_r(x)| \leq C r^{-3}, \quad (29)$$

$$\int_{|x|>r} \rho_0 \leq C r^{-3}, \quad (30)$$

$$\int_{|x|>r} \rho_0^{5/3} \leq C r^{-7}, \quad (31)$$

$$\text{Tr}(-\Delta \eta_r \gamma_0 \eta_r) \leq C(r^{-7} + \lambda^{-2} r^{-5}), \quad \forall \lambda \in (0, 1/2]. \quad (32)$$

We emphasize that, while (28) and (29) are straightforward consequences of (22), the bounds (32), (31) and (30) rely on the outside L^1 bound from Lemma 7 and the outside kinetic energy bound from Lemma 10. Recall that the smooth cut-off function η_r is defined in (8) and depends on the parameter λ .

Proof. The proofs of (28) and (29) can be carried out similarly to [4, Proof of Lemma 20]. Note that, in contrast to the corresponding statement in [4, Lemma 20], in (29) we claim a bound on $|\Phi_r(x)|$. This, however, follows in the same way by applying [4, Lemma 19] both to Φ_r and to $-\Phi_r$.

Note that there is an alternative, simpler proof of (28) and (29) based on the spherical symmetry of ρ_0 , which follows from the convexity of the Müller functional. It implies that $\Phi_r(x) - \Phi_r^{\text{TF}}(x) = |x|^{-1} \int_{|y|<r} (\rho_0 - \rho^{\text{TF}}) dy$ for $|x| \geq r$, so that (28) follows immediately from (22) and (29) follows from (28) and a corresponding bound for $\Phi_r^{\text{TF}}(x)$.

Now we prove (30) and (32). By (28) and the bound $\rho^{\text{TF}} \leq C|x|^{-6}$, we have

$$\begin{aligned} \int_{r/3 < |x| < r} \rho_0 &= \int_{|x|<r} (\rho_0 - \rho^{\text{TF}}) - \int_{|x|<r/3} (\rho_0 - \rho^{\text{TF}}) + \int_{r/3 < |x| < r} \rho^{\text{TF}} \\ &\leq \beta r^{-3} + \beta (r/3)^{-3} + C r^{-3} \leq C r^{-3}. \end{aligned} \quad (33)$$

Inserting this and the bound (29) into the bound from Lemma 10, we obtain

$$\begin{aligned} \text{Tr}(-\Delta \eta_r \gamma_0 \eta_r) &\leq C(1 + (\lambda r)^{-2}) \int \chi_{(1-\lambda)r}^+ \rho_0 \\ &\quad + C \lambda r^3 \sup_{|z| \geq (1-\lambda)r} [\Phi_{(1-\lambda)r}(z)]_+^{5/2} + C \sup_{|z| \geq r} [|z| \Phi_r(z)]_+^{7/3} \\ &\leq C \left(\lambda^{-2} r^{-2} \int \chi_r^+ \rho_0 + \lambda^{-2} r^{-5} + r^{-7} \right). \end{aligned} \quad (34)$$

In (34), replacing r by $r/3$ and using again (33) we get

$$\mathrm{Tr}(-\Delta\eta_{r/3}\gamma_0\eta_{r/3}) \leq C\left(\lambda^{-2}r^{-2} \int \chi_r^+ \rho_0 + \lambda^{-2}r^{-5} + r^{-7}\right). \quad (35)$$

From the exterior bound from Lemma 7, replacing r by $r/3$ and choosing $s = r$ (this choice is not optimal but sufficient), we find that

$$\begin{aligned} \int \chi_{r/3}^+ \rho_0 &\leq C \int_{r/3 < |x| < (1+\lambda)^2 r/3} \rho_0 + C \left(\sup_{|z| \geq r/3} [|z| \Phi_{r/3}(z)]_+ + \lambda^{-2}r^{-1} \right) \\ &\quad + C \left(r^2 \mathrm{Tr}(-\Delta\eta_{r/3}\gamma_0\eta_{r/3}) \right)^{3/5} + C \left(r^2 \mathrm{Tr}(-\Delta\eta_{r/3}\gamma_0\eta_{r/3}) \right)^{1/3}. \end{aligned}$$

Inserting (29), (33) and (34) into the latter estimate leads to

$$\begin{aligned} \int \chi_r^+ \rho_0 &\leq \int \chi_{r/3}^+ \rho_0 \leq C(r^{-3} + \lambda^{-2}r^{-1}) \\ &\quad + C \left(\lambda^{-2} \int \chi_r^+ \rho_0 + \lambda^{-2}r^{-3} + r^{-5} \right)^{3/5} \\ &\quad + C \left(\lambda^{-2} \int \chi_r^+ \rho_0 + \lambda^{-2}r^{-3} + r^{-5} \right)^{1/3} \end{aligned}$$

which implies (30) immediately (we can choose $\lambda = 1/2$ on the right side). Inserting (30) into (34) we obtain (32).

Finally, from (32) and the kinetic Lieb–Thirring inequality, we have

$$\int_{|x| > r} \rho_0^{5/3} \leq \int (\eta_{r/3}^2 \rho_0)^{5/3} \leq C \mathrm{Tr}(-\Delta\eta_{r/3}\gamma_0\eta_{r/3}) \leq C(r^{-7} + \lambda^{-2}r^{-5}).$$

which implies (31) (we can choose $\lambda = 1/2$ on the right side). \square

Step 2. Now we introduce the exterior Thomas–Fermi energy functional

$$\mathcal{E}_r^{\mathrm{TF}}(\rho) = c^{\mathrm{TF}} \int \rho^{5/3} - \int V_r \rho + D(\rho), \quad V_r(x) = \chi_r^+ \Phi_r(x)$$

with c_{TF} from (2).

Lemma 17. *The functional $\mathcal{E}_r^{\mathrm{TF}}(\rho)$ has a unique minimizer ρ_r^{TF} over*

$$0 \leq \rho \in L^{5/3}(\mathbb{R}^3) \cap L^1(\mathbb{R}^3), \quad \int \rho \leq \int \chi_r^+ \rho_0.$$

This minimizer is supported on $\{|x| \geq r\}$ and satisfies the Thomas–Fermi equation

$$\frac{5c^{\mathrm{TF}}}{3} \rho_r^{\mathrm{TF}}(x)^{2/3} = [\varphi_r^{\mathrm{TF}}(x) - \mu_r^{\mathrm{TF}}]_+$$

*with $\varphi_r^{\mathrm{TF}}(x) = V_r(x) - \rho_r^{\mathrm{TF}} * |x|^{-1}$ and a constant $\mu_r^{\mathrm{TF}} \geq 0$. Moreover, if (22) holds true for some $\beta, D \in (0, 1]$, then*

$$\int (\rho_r^{\mathrm{TF}})^{5/3} \leq Cr^{-7}, \quad \forall r \in (0, D]. \quad (36)$$

The proof of this lemma is identical to that of [4, Lemma 21] and is omitted.

Step 3. Now we compare ρ_r^{TF} with $\chi_r^+ \rho^{\mathrm{TF}}$.

Lemma 18. *We can choose a universal constant $\beta > 0$ small enough such that, if (22) holds true for some $D \in [Z^{-1/3}, 1]$, then $\mu_r^{\text{TF}} = 0$ and*

$$\begin{aligned} |\varphi_r^{\text{TF}}(x) - \varphi^{\text{TF}}(x)| &\leq C(r/|x|)^\zeta |x|^{-4}, \\ |\rho_r^{\text{TF}}(x) - \rho^{\text{TF}}(x)| &\leq C(r/|x|)^\zeta |x|^{-6} \end{aligned}$$

for all $r \in [Z^{-1/3}, D]$ and for all $|x| \geq r$. Here $\zeta = (\sqrt{73} - 7)/2 \approx 0.77$.

The proof of this lemma is identical to that of [4, Lemma 22] and is omitted.

Step 4. In this step, we compare ρ_r^{TF} with $\chi_r^+ \rho_0$.

Lemma 19. *Let $\beta > 0$ be as in Lemma 18. Assume that (22) holds true for some $D \in [Z^{-1/3}, 1]$. Then*

$$D(\chi_r^+ \rho_0 - \rho_r^{\text{TF}}) \leq Cr^{-7+b}, \quad \forall r \in [Z^{-1/3}, D],$$

where $b = 1/3$.

Proof. The proof of this lemma is analogous, but somewhat more involved than the proof of Lemma 14. The strategy is to bound $\mathcal{E}_r^{\text{RHF}}(\eta_r \gamma_0 \eta_r)$ from above and below using the semi-classical estimates from Lemma 11. The main term in both bounds is $\mathcal{E}_r^{\text{TF}}(\rho_r^{\text{TF}})$, but in the lower bound we will get an additional term $D(\chi_r^+ \rho_0 - \rho_r^{\text{TF}})$. The error terms in the upper and lower bounds will then give the desired bound in the lemma.

Upper bound. We shall prove that

$$\mathcal{E}_r^{\text{RHF}}(\eta_r \gamma_0 \eta_r) \leq \mathcal{E}_r^{\text{TF}}(\rho_r^{\text{TF}}) + Cr^{-7} \left(r^{2/3} + \lambda^{-2} r^2 + \lambda \right). \quad (37)$$

We use Lemma 11 (ii) with $V_r' \equiv \chi_{r+s}^+ \varphi_r^{\text{TF}}$, $s \leq r$ to be chosen later and g spherically symmetric to obtain a density matrix γ_r as in the statement. Since $\mu_r^{\text{TF}} = 0$ by Lemma 18, we deduce from the Thomas–Fermi equation in Lemma 17 that

$$\rho_{\gamma_r} = \frac{5}{2} L_{\text{sc}} \left(\chi_{r+s}^+ (\varphi_r^{\text{TF}})^{3/2} \right) * g^2 = (\chi_{r+s}^+ \rho_r^{\text{TF}}) * g^2.$$

Note that ρ_{γ_r} is supported in $\{|x| \geq r\}$ and

$$\text{Tr } \gamma_r = \int \rho_{\gamma_r} = \int \chi_{r+s}^+ \rho_r^{\text{TF}} \leq \int \rho_r^{\text{TF}} \leq \int \chi_r^+ \rho_0.$$

Thus, we may apply Lemma 9 and obtain

$$\mathcal{E}_r^{\text{RHF}}(\eta_r \gamma_0 \eta_r) \leq \mathcal{E}_r^{\text{RHF}}(\gamma_r) + \mathcal{R}. \quad (38)$$

By the semiclassical estimate from Lemma 11 (ii)

$$\begin{aligned}
\mathcal{E}_r^{\text{RHF}}(\gamma_r) &\leq \frac{3}{2}L_{\text{sc}} \int [V_r']_+^{5/2} + Cs^{-2} \int [V_r']_+^{3/2} - \int \Phi_r ((\chi_{r+s}^+ \rho_r^{\text{TF}}) * g^2) \\
&\quad + D(\rho_r^{\text{TF}} * g^2) \\
&\leq \frac{3}{2}L_{\text{sc}} \int [\varphi_r^{\text{TF}}]_+^{5/2} - \int \Phi_r \rho_r^{\text{TF}} + D(\rho_r^{\text{TF}}) \\
&\quad + Cs^{-2} \int \rho_r^{\text{TF}} + \int (\Phi_r - \Phi_r * g^2) \chi_{r+s}^+ \rho_r^{\text{TF}} + \int_{r \leq |x| \leq r+s} \Phi_r \rho_r^{\text{TF}} \\
&= \mathcal{E}_r^{\text{TF}}(\rho_r^{\text{TF}}) + Cs^{-2} \int \rho_r^{\text{TF}} + \int_{r \leq |x| \leq r+s} \Phi_r \rho_r^{\text{TF}},
\end{aligned}$$

where we have used the convexity of D in the second inequality. The equality in the last line holds, since $\Phi_r(x)$ is harmonic when $|x| \geq r$ and g is chosen spherically symmetric.

According to (30) in Lemma 16 we have

$$\int \rho_r^{\text{TF}} \leq \int \chi_r^+ \rho_0 \leq Cr^{-3}.$$

We now use the fact that $\rho_r^{\text{TF}}(x) \leq C|x|^{-6}$ for all $|x| \geq r$, which follows from Lemma 18 because of the corresponding bound for ρ^{TF} . (In fact, the claimed upper bound does not need the full strength of Lemma 18, so as part of the proof one shows that $\varphi_r^{\text{TF}}(x) \leq Cr^{-4}$ for $|x| \geq r$ and therefore the claimed bound follows from the Thomas–Fermi equation for ρ_r^{TF} .) Thus, using (29) in Lemma 16,

$$\int_{r \leq |x| \leq r+s} \Phi_r \rho_r^{\text{TF}} \leq Cr^{-3} \int_{r \leq |x| \leq r+s} |x|^{-1} \rho_r^{\text{TF}} \leq Cr^{-8}s.$$

Optimizing over s (which leads to $s \sim r^{5/3}$) we obtain

$$\mathcal{E}_r^{\text{RHF}}(\gamma_r) \leq \mathcal{E}_r^{\text{TF}}(\rho_r^{\text{TF}}) + Cr^{-7+2/3}. \quad (39)$$

Finally, we estimate \mathcal{R} using Lemma 16 and obtain

$$\begin{aligned}
\mathcal{R} &\leq C(1 + (\lambda r)^{-2})r^{-3} + C\lambda r^3(r^{-4})^{5/2} + C(r^{-7} + \lambda^{-2}r^{-5})^{1/2}(r^{-3})^{1/2} \\
&\leq C(\lambda^{-2}r^{-5} + \lambda r^{-7}).
\end{aligned}$$

Combining this with (38) and (39) we obtain the claimed upper bound (37).

Lower bound. We shall prove that

$$\mathcal{E}_r^{\text{RHF}}(\eta_r \gamma_0 \eta_r) \geq \mathcal{E}_r^{\text{TF}}(\rho_r^{\text{TF}}) + D(\eta_r^2 \rho_0 - \rho_r^{\text{TF}}) - Cr^{-7+1/3} \quad (40)$$

We use Lemma 11 (i) in a way similar to the proof of Lemma 14 to obtain

$$\begin{aligned}
\mathcal{E}_r^{\text{RHF}}(\eta_r \gamma_0 \eta_r) &= \text{Tr}((-\Delta - \varphi_r^{\text{TF}}) \eta_r \gamma_0 \eta_r) + D(\eta_r^2 \rho_0 - \rho_r^{\text{TF}}) - D(\rho_r^{\text{TF}}) \\
&\geq -L_{\text{sc}} \int [\varphi_r^{\text{TF}}]_+^{5/2} - C s^{-2} \int \eta_r^2 \rho_0 \\
&\quad - C \left(\int [\varphi_r^{\text{TF}}]_+^{5/2} \right)^{3/5} \left(\int [\varphi_r^{\text{TF}} - \varphi_r^{\text{TF}} * g^2]_+^{5/2} \right)^{2/5} \\
&\quad + D(\eta_r^2 \rho_0 - \rho_r^{\text{TF}}) - D(\rho_r^{\text{TF}}) \\
&= \mathcal{E}_r^{\text{TF}}(\rho_r^{\text{TF}}) + D(\eta_r^2 \rho_0 - \rho_r^{\text{TF}}) - C s^{-2} \int \eta_r^2 \rho_0 \\
&\quad - C \left(\int [\varphi_r^{\text{TF}}]_+^{5/2} \right)^{3/5} \left(\int [\varphi_r^{\text{TF}} - \varphi_r^{\text{TF}} * g^2]_+^{5/2} \right)^{2/5}.
\end{aligned}$$

The last identity used the Thomas–Fermi equations similarly as in (27).

In order to control the remainder terms we note that by Lemmas 16 and 17 we have

$$\int \eta_r^2 \rho_0 \leq C r^{-3}, \quad \int [\varphi_r^{\text{TF}}]_+^{5/2} = C \int (\rho_r^{\text{TF}})^{5/3} \leq C r^{-7}.$$

In order to bound the convolution term we use, as in the proof of Lemma 14 the fact that $|x|^{-1} - |x|^{-1} * g^2 \geq 0$, and therefore also $\rho_r^{\text{TF}} * (|x|^{-1} - |x|^{-1} * g^2) \geq 0$. Since $\varphi_r^{\text{TF}} = \chi_r^+ \Phi_r - \rho_r^{\text{TF}} * |x|^{-1}$, we conclude that

$$\varphi_r^{\text{TF}} - \varphi_r^{\text{TF}} * g^2 \leq \chi_r^+ \Phi_r - (\chi_r^+ \Phi_r) * g^2.$$

Since Φ_r is harmonic outside a ball of radius r and g is spherically symmetric, $\chi_r^+ \Phi_r - (\chi_r^+ \Phi_r) * g^2$ is supported in $\{r - s \leq |x| \leq r + s\}$ and, by Lemma 16, its absolute value is bounded by $C r^{-4}$. Thus,

$$[\varphi_r^{\text{TF}} - \varphi_r^{\text{TF}} * g^2]_+ \leq C r^{-4} \mathbf{1}(r - s \leq |\cdot| \leq r + s)$$

and therefore

$$\int [\varphi_r^{\text{TF}} - \varphi_r^{\text{TF}} * g^2]_+^{5/2} \leq C r^{-8} s$$

To summarize, we have shown that

$$\mathcal{E}_r^{\text{RHF}}(\eta_r \gamma_0 \eta_r) \geq \mathcal{E}_r^{\text{TF}}(\rho_r^{\text{TF}}) + D(\eta_r^2 \rho_0 - \rho_r^{\text{TF}}) - C \left(s^{-2} r^{-3} + r^{-37/5} s^{2/5} \right).$$

Optimizing over s (which leads to $s \sim r^{11/6}$) we obtain (40).

Conclusion. Combining (37) and (40) we infer that

$$D(\eta_r^2 \rho_0 - \rho_r^{\text{TF}}) \leq C r^{-7} \left(r^{1/3} + \lambda^{-2} r^2 + \lambda \right).$$

The next step is to replace η_r^2 by χ_r^+ . By using the Hardy–Littewood–Soloblev inequality and (31), we get

$$\begin{aligned}
D(\chi_r^+ \rho_0 - \eta_r^2 \rho_0) &\leq D(\mathbf{1}((1 + \lambda)r \geq |x| \geq r) \rho_0) \\
&\leq C \|\mathbf{1}((1 + \lambda)r \geq |x| \geq r) \rho_0\|_{L^{6/5}}^2 \\
&\leq C \left(\int \chi_r^+ \rho_0^{5/3} \right)^{6/5} \left(\int_{(1+\lambda)r \geq |x| \geq r} \right)^{7/15} \\
&\leq C (r^{-7})^{6/5} (\lambda r^3)^{7/15} = C \lambda^{7/15} r^{-7}.
\end{aligned}$$

Therefore,

$$\begin{aligned} D(\chi_r^+ \rho_0 - \rho_r^{\text{TF}}) &\leq 2D(\chi_r^+ \rho_0 - \eta_r^2 \rho_0) + 2D(\eta_r^2 \rho_0 - \rho_r^{\text{TF}}) \\ &\leq Cr^{-7} \left(\lambda^{7/15} + r^{1/3} + \lambda^{-2} r^2 \right). \end{aligned}$$

This bound is valid for all $\lambda \in (0, 1/2]$ and by optimizing over λ (which leads to $\lambda \sim r^{30/37}$) we obtain

$$D(\chi_r^+ \rho_0 - \rho_r^{\text{TF}}) \leq Cr^{-7+1/3}.$$

This is the desired estimate. \square

Step 5. Now we are ready to conclude. The argument is similar to that in [4, Lemma 17], but for the convenience of the reader we provide the details.

Proof of Lemma 15. Let $r \in [Z^{-1/3}, D]$ and $|x| \geq r$. As in [15, Eq. (97)], we can decompose

$$\begin{aligned} \Phi_{|x|}(x) - \Phi_{|x|}^{\text{TF}}(x) &= \varphi_r^{\text{TF}}(x) - \varphi^{\text{TF}}(x) + \int_{|y|>|x|} \frac{\rho_r^{\text{TF}}(y) - \rho^{\text{TF}}(y)}{|x-y|} dy, \\ &\quad + \int_{|y|<|x|} \frac{\rho_r^{\text{TF}}(y) - (\chi_r^+ \rho_0)(y)}{|x-y|} dy. \end{aligned}$$

By Lemma 18, we have

$$|\varphi_r^{\text{TF}}(x) - \varphi^{\text{TF}}(x)| \leq C(r/|x|)^\zeta |x|^{-4}$$

and

$$\int_{|y|>|x|} \frac{|\rho_r^{\text{TF}}(y) - \rho^{\text{TF}}(y)|}{|x-y|} dy \leq C \int_{|y|>|x|} \frac{(r/|y|)^\zeta |y|^{-6}}{|x-y|} dy \leq C(r/|x|)^\zeta |x|^{-4}.$$

Moreover, from (21), (31), (36) and Lemma 19, we get

$$\begin{aligned} \left| \int_{|y|<|x|} \frac{\rho_r^{\text{TF}}(y) - (\chi_r^+ \rho_0)(y)}{|x-y|} dy \right| &\leq C \|\rho_r^{\text{TF}} - \chi_r^+ \rho_0\|_{L^{5/3}}^{5/6} \left(|x| D(\rho_r^{\text{TF}} - \chi_r^+ \rho_0) \right)^{1/12} \\ &\leq C(r^{-7})^{1/2} (|x| r^{-7+b})^{1/12} \\ &= C|x|^{-4+b/12} (|x|/r)^{4+1/12-b/12}, \end{aligned}$$

Thus in summary, for all $r \in [Z^{-1/3}, D]$ and $|x| \geq r$, we have

$$|\Phi_{|x|}(x) - \Phi_{|x|}^{\text{TF}}(x)| \leq C(r/|x|)^\zeta |x|^{-4} + C(|x|/r)^5 |x|^{-4+b/12}. \quad (41)$$

Now let us conclude using (41). We choose a constant $\delta \in (0, 1)$ sufficiently small such that

$$\frac{1+\delta}{1-\delta} \left(\frac{49}{36} - a \right) < \frac{49}{36} \quad (42)$$

and

$$\frac{b}{12} - \frac{10\delta}{1-\delta} > 0. \quad (43)$$

We recall that a and b are the constants from Lemmas 14 and 19, respectively. We distinguish two cases.

Case 1: $D^{1+\delta} \leq Z^{-1/3}$. In this case, we simply use the initial step. Indeed, for all

$$|x| \leq D^{1-\delta} \leq (Z^{-1/3})^{(1-\delta)/(1+\delta)},$$

by Lemma 14 we have

$$|\Phi_{|x|}(x) - \Phi_{|x|}^{\text{TF}}(x)| \leq C_1 Z^{49/36-a} |x|^{1/12} \leq C_1 |x|^{1/12-3\frac{1+\delta}{1-\delta}(49/36-a)}. \quad (44)$$

Note that

$$\frac{1}{12} - 3 \times \frac{49}{36} = -4$$

Therefore, (42) implies that

$$\frac{1}{12} - \frac{3(1+\delta)}{1-\delta} \left(\frac{49}{36} - a \right) > -4.$$

Case 2: $D^{1+\delta} \geq Z^{-1/3}$. In this case, we use (41) with $r = D^{1+\delta}$. For all $D \leq |x| \leq D^{1-\delta}$ we have

$$|x|^{2\delta/(1-\delta)} \leq r/|x| \leq |x|^\delta.$$

Therefore, (41) implies that

$$|\Phi_{|x|}(x) - \Phi_{|x|}^{\text{TF}}(x)| \leq C|x|^{-4+\zeta\delta} + C|x|^{-4+b/12-10\delta/(1-\delta)}. \quad (45)$$

Both exponents of $|x|$ are strictly greater than -4 according to (43).

In summary, from (44) and (45), we conclude that in both cases,

$$|\Phi_{|x|}(x) - \Phi_{|x|}^{\text{TF}}(x)| \leq C|x|^{-4+\varepsilon}, \quad \forall D \leq |x| \leq D^{1-\delta}.$$

with

$$\varepsilon := \min \left\{ \frac{1}{12} - \frac{3(1+\delta)}{1-\delta} \left(\frac{49}{36} - a \right) + 4, \frac{b}{12} - \frac{10\delta}{1-\delta}, \zeta\delta \right\} > 0.$$

This completes the proof of Lemma 15. \square

9. PROOF OF THE MAIN THEOREM

Now we prove the uniform bound $N \leq Z + C$. The argument is identical to the proof of Theorem 1 in [4], but we repeat it below for the convenience of the reader.

Proof of Theorem 1. Since we have proved $N \leq 2Z + C(Z^{2/3} + 1)$ in Lemma 8, it remains to consider the case $N \geq Z \geq 1$. By Theorem 2, we can find universal constants $C, \varepsilon, D > 0$ such that

$$|\Phi_{|x|}(x) - \Phi_{|x|}^{\text{TF}}(x)| \leq C|x|^{-4+\varepsilon}, \quad \forall |x| \leq D.$$

In particular, (22) holds true with a universal constant $\beta = CD^\varepsilon$. We can choose D sufficiently small such that $D \leq 1$ and $\beta \leq 1$, which allows us to apply Lemma 16. Then using (28) and (30) with $r = D$, we find that

$$\int_{|x|>D} \rho_0 + \left| \int_{|x|<D} (\rho_0 - \rho^{\text{TF}}) \right| \leq C.$$

Combining with $\int \rho^{\text{TF}} = Z$, we obtain the ionization bound

$$N = \int \rho_0 = \int_{|x|>D} \rho_0 + \int_{|x|<D} (\rho_0 - \rho^{\text{TF}}) + \int_{|x|<D} \rho^{\text{TF}} \leq C + Z. \quad \square$$

The proofs of Theorems 2 and 3 follow from Lemma 13 in the same way as [4, Theorems 1 and 2] follow from [4, Lemma 15].

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